A GENERAL THEORY OF ENERGY PARTITION WITH APPLICATIONS TO QUANTUM THEORY.

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Introduction.—The principle of the equipartition of energy was one of the most definite and important results of the older statistical mechanics, and the contradiction between this principle and actual experimental findings, in particular in the case of the distribution of energy in the hohlraum, has led many physicists to believe that the underlying structure of statistical mechanics must itself be false. More specifically, since statistical mechanics is most conveniently based on the equations of motion in the Hamiltonian form, many critics of the older statistical mechanics have come to the conclusion that Hamilton's equations are themselves incorrect, and indeed some extremists have gone so far as to believe that any set of equations would be incorrect which, like those of Hamilton, take time as a *continuous* variable, since they think that time has in reality an atomic nature and that all changes in configuration take place by jumps.

It is well known, however, as shown by the work of Helmholtz, Maxwell, J. J. Thomson, Planck and others[1] that for all *macroscopic* systems whose behavior is completely known it has been found possible to throw the equations of motion into the Hamiltonian form, provided we make suitable choices for the functional relationships between the generalized coördinates $\phi_1\phi_2\cdots\phi_n$, the generalized velocities $\dot{\phi}_1\dot{\phi}_2\cdots\dot{\phi}_n$,

[1] The appended references may be consulted as an evidence of the general applicability of the principle of least action in all *known* fields of dynamics. The methods of transposing the equations of motion from the form demanded by the principle of least action to the Hamiltonian form are well known. In carrying out this transformation it should be remembered that the system must be taken inclusive enough so as not to be acted on by external forces.

See Helmholtz, (Vorlesungen über theoretische Physik); note the development of electromagnetic theory from a dynamical basis by Maxwell (Treatise on Electricity and Magnetism) and by Larmor (Phil. Trans., *A*–719 (1884), p. 694 (1895)); the treatment of various fields by Sir J. J. Thomson (Applications of Dynamics to Physics and Chemistry, Macmillan, 1888); the presentation of optical theory on a dynamical basis by Maclaurin (The Theory of Light, Cambridge, 1908); and considerable work in newer fields based on the principle of least action by Planck (Ann. d. Physik, *26*, 1 (1908)), Herglotz (Ann. d. Physik, *36*, 493 (1911)), de Wisniewski (Ann. d. Physik, *40*, 668 (1913)), Tolman (Phil. Mag., 28, 583 (1914), and The Theory of the Relativity of Motion, University of California Press, 1917).

the generalized momenta $\psi_1\psi_2\cdots\psi_n$, and the Hamiltonian function H. For this reason the writer is inclined to believe that in the case of the ensembles of *microscopic* systems considered by statistical mechanics it is very unwise to abandon the Hamiltonian equations of motion unless we are absolutely forced to it. It should also be noted that the variables involved in an equation of motion can always be considered as having ultimately a continuous nature, since apparent jumps in configuration can always be accounted for by the assumption of immeasurably high velocities. Such considerations make it necessary to investigate the whole structure of statistical mechanics and determine if the Hamiltonian equations of motion actually do necessitate the principle of the equipartition of energy.

We shall find that the principle of the equipartition of energy is not in the least to be regarded as a necessary consequence of Hamilton's equations, but has been derived from those equations merely because energy has, quite unnecessarily, always been taken as a homogeneous quadratic function of the generalized coördinates. We shall be able, furthermore, to derive a new and very general equipartition law for the equipartition of a function, which reduces to energy for the special case that energy does happen to be a quadratic function of the coördinates. Our methods will further permit us to study the actual partition of energy with various functional relations between energy and the coördinates, and we shall consider a number of interesting systems where energy is not equiparted which have hitherto been neglected. Finally, in the case of the hohlraum, we shall consider a functional relation between energy and the coördinates which does lead to the partition of energy actually found experimentally, and also leads to the absorption and evolution of radiant energy in a relatively discontinuous manner in amounts $h\nu$, thus agreeing with the photoelectric and inverse photoelectric effects.

This treatment of the hohlraum which we shall present leads to the expression

$$\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

for the average energy associated with a mode of vibration of frequency ν, in a hohlraum which has come to thermodynamic equilibrium at temperature T. This expression is known to agree at least substantially with the experimental facts and is the expression proposed by most forms of the so-called quantum theory of radiation. Our treatment of the hohlraum differs, however, from previous forms of quantum theory in not disturbing

in the least the fundamental structure of the familiar classical statistical mechanics. In essence, our development adopts the essentials of the older statistical mechanics, and merely grafts on to it the new idea, that energy is not necessarily a quadratic function of the generalized coördinates and momenta which appear in the equations of motion in the Hamiltonian form.[1] The methods of attack, which are here considered, are moreover much more general than any hitherto employed by the quantum theory, since they permit a study of the partition of energy for an infinite variety of forms of relation between energy and the coordinates. Thus in the present article, we shall consider the energy partition in a number of systems besides those which can be treated by the quantum theory, including for example the partition of energy in a gas subjected to the action of gravity. Indeed it is to be specially emphasized that we shall find the structure of statistical mechanics quite big enough to account for any desired number of different modes of energy distribution besides the particular one proposed by the quantum theory.[2]

PART I. STATISTICAL MECHANICS.

The Equations of Motion.—Consider an isolated system whose state is defined by the n generalized coördinates $(\phi_1\phi_2\cdots\phi_n)$ and the corresponding momenta $(\psi_1\psi_2\cdots\psi_n)$. Then in accordance with Hamilton's equations we may write the equations of motion for this system in the form

$$\begin{aligned} \frac{\partial H}{\partial \phi_1} &= -\dot{\psi}_1, \quad \frac{\partial H}{\partial \phi_2} = -\dot{\psi}_2, \quad \cdots, \\ \frac{\partial H}{\partial \psi_1} &= \dot{\phi}_1, \quad \frac{\partial H}{\partial \psi_2} = \dot{\phi}_2, \quad \cdots, \end{aligned} \tag{1}$$

where H is the Hamiltonian function, and $\dot{\psi}_1 = (d\psi_1/dt)$, etc.

Geometrical Representation.—Employing the methods so successfully used by Jeans,[3] we may now think of the state of the system at any instant as determined by the position of a point plotted in a $2n$-dimensional space. Suppose now we have a large number of systems of the same structure but differing in state, then for each system we should have at each instant a corresponding point in our $2n$-dimensional space, and as the systems change in state, in accordance with equations (1), the points will describe stream lines in the generalized space.

[1] The investigations already referred to show the possibility of a variety of functional relationships between energy and the generalized coördinates and momenta.

[2] This fact might assume unexpected importance if more accurate measurements of the distribution of energy in the hohlraum should lead us to discard Planck's formula as experimentally correct.

[3] The Dynamical Theory of Gases, 2d edition, Cambridge, 1916.

The Maintenance of Uniform Density.—Suppose now that the points were originally distributed uniformly throughout the space, then it is a necessary consequence of our equations of motion that the distribution will remain uniform. To show this, we note that we may write for the rate at which the density at any point is increasing:

$$\frac{d\rho}{dt} = -\rho\left(\frac{\partial\dot{\phi}_1}{\partial\phi_1}+\frac{\partial\dot{\phi}_2}{\partial\phi_2}+\frac{\partial\dot{\phi}_3}{\partial\phi_3}+\cdots+\frac{\partial\dot{\psi}_1}{\partial\psi_1}+\frac{\partial\dot{\psi}_2}{\partial\psi_2}+\frac{\partial\dot{\psi}_3}{\partial\psi_3}+\cdots\right),$$

and since our equations of motion (1) evidently lead to the relations

$$\frac{\partial\dot{\phi}_1}{\partial\phi_1}+\frac{\partial\dot{\psi}_1}{\partial\psi_1}=0,$$

$$\frac{\partial\dot{\phi}_2}{\partial\phi_2}+\frac{\partial\dot{\psi}_2}{\partial\psi_2}=0, \text{ etc.},$$

we see that the original uniform density will not change.

This important result means that there is no tendency for the representative points to crowd into any particular part of the generalized space, and hence if we start some one system going and plot its state in our generalized space, we may assume,[1] that, after an indefinite lapse of time, its representative point is equally likely to be in any one of the infinitesimal elements of equal volume ($d\phi_1 d\phi_2 d\phi_3\cdots d\psi_1 d\psi_2 d\psi_3\cdots$) into which we can divide our generalized space, provided of course the coordinates for the location of this element correspond to the actual energy content of our system.

Microscopic State.—As a convenient nomenclature, we shall say that a statement of the particular element of volume ($d\phi_1 d\phi_2 d\phi_3\cdots d\psi_1 d\psi_2 d\psi_3\cdots$) in which the representative point for our given system is found is a specification of the *microscopic state of the system. And the principle, which we have just obtained, states that all the different microscopic states possible have the same probability.*

Statistical State.—Let us suppose now that our system is a thermodynamic one composed of a large number of identical elements, such as atoms, molecules, oscillators, modes of vibration, etc. We may let N_A, N_B, N_C, etc., be the number of elements of each of the different kinds A, B, C, etc., which go to make up the complete system, and may consider our original $2n$ coördinates and momenta as divided up among these different elements.

For such a thermodynamic system we shall be particularly interested in the number of elements of any particular kind A which have coordinates and momenta falling in a given infinitesimal range ($d_A\phi_1\, d_A\phi_2$

[1] It is not within the scope of our present undertaking to enter into the vexed discussions as to the validity of this assumption.

$\cdots\, d_A\psi_1\, d_A\psi_2 \cdots$) and this determines what we shall call the *statistical state of the system.*

The microscopic state of the system and the statistical state differ in that the former determines the coördinates and momenta for each individual element, while the latter only states the number of elements of the different kinds which have coördinates and momenta of a given magnitude, without making any distinction as to which particular elements are taken to supply a quota. Thus we see that, corresponding to a given statistical state of the system, there will be a large number of microscopic states, and, since we have already seen that all microscopic states are equally probable, we obtain the important conclusion that the probability of occurrence for a given statistical state is proportional to the number of microscopic states to which it corresponds.

Probability of a Given Statistical State.—Let us now specify a given statistical state by stating that ${}_1N_A\ {}_2N_A\ {}_3N_A \cdots {}_1N_B\ {}_2N_B\ {}_3N_B \cdots {}_1N_C\ {}_2N_C\ {}_3N_C \cdots$, etc., are the number of elements of each of the kinds, which have values of coördinates and momenta which fall in the particular infinitesimal ranges Nos. $1A$, $2A$, $3A$, $\cdots$, $1B$, $2B$, $3B$, $\cdots$, etc. Then it is evident from the principles of permutation that the number of microscopic states corresponding to this statistical state will be:

$$W = \frac{\lfloor N_A \lfloor N_B \lfloor N_C \cdots}{\lfloor {}_1N_A \lfloor {}_2N_A \lfloor {}_3N_A \cdots \lfloor {}_1N_B \lfloor {}_2N_B \cdots \lfloor {}_3N_B \lfloor {}_1N_C \lfloor {}_2N_C \lfloor {}_3N_C \cdots} \tag{2}$$

and we shall call this the *probability* of the given statistical state, without bothering to introduce any proportionality factor.

Let us assume now that each of the numbers ${}_1N_A\ {}_2N_B$, etc., are large enough so that we may apply the Stirling Formula,

$$\lfloor N = \sqrt{2\pi N}\left(\frac{N}{e}\right)^N. \tag{3}$$

Introducing into (2), taking the logarithm of W for greater convenience, and omitting negligible terms we obtain:

$$\begin{aligned}\log W = &- N_A\left(\frac{{}_1N_A}{N_A}\log\frac{{}_1N_A}{N_A} + \frac{{}_2N_A}{N_A}\log\frac{{}_2N_A}{N_A} + \frac{{}_3N_A}{N_A}\log\frac{{}_3N_A}{N_A} + \cdots\right)\\ &- N_B\left(\frac{{}_1N_B}{N_B}\log\frac{{}_1N_B}{N_B} + \frac{{}_2N_B}{N_B}\log\frac{{}_2N_B}{N_B} + \frac{{}_3N_B}{N_B}\log\frac{{}_3N_B}{N_B} + \cdots\right)\\ &- N_C\left(\frac{{}_1N_C}{N_C}\log\frac{{}_1N_C}{N_C} + \frac{{}_2N_C}{N_C}\log\frac{{}_2N_C}{N_C} + \frac{{}_3N_C}{N_C}\log\frac{{}_3N_C}{N_C} + \cdots\right)\\ &- \text{etc.}\end{aligned} \tag{4}$$

The ratios ${}_1N_A/N_A$, ${}_2N_A/N_A$, etc., evidently give the probability that

any particular element of the kind in question shall have values of the coördinates and momenta falling within particular infinitesimal ranges ($d_A\phi_1\ d_A\phi_2 \cdots d_A\psi_1\ d_A\psi_2 \cdots$) Nos. 1 A, 2 A, etc., provided the system is in the given statistical state. Let us denote these ratios by the symbols ${}_1w_A$, ${}_2w_A$, etc.,

$$ {}_iw_A = \frac{{}_iN_A}{N_A}, \quad {}_iw_B = \frac{{}_iN_B}{N_B}, \quad {}_iw_C = \frac{{}_iN_C}{N_C}, \quad \text{etc.} \tag{5} $$

Then we may rewrite equation (4) in the form

$$ \log W = -N_A \sum_{i=1,2,3,\ldots} {}_iw_A \log {}_iw_A - N_B \sum_{i=1,2,3,\ldots} {}_iw_B \log {}_iw_B - N_C \sum_{i=1,2,3,\ldots} {}_iw_C \log {}_iw_C - \cdots. \tag{6} $$

State of Maximum Probability.—Having obtained this expression for the probability of a given statistical state, let us determine what particular state is the most probable with a given energy content. The condition of maximum probability will evidently be:

$$ \delta \log W = -N_A \Sigma(\log {}_iw_A + 1)\delta\, {}_iw_A - N_B \Sigma(\log {}_iw_B + 1)\delta\, w_B \cdots = 0. \tag{7} $$

The variation δ, however, cannot be carried out entirely arbitrarily since the number of elements of any particular kind cannot be varied and the total amount of energy is to be a constant.

In accordance with equations (5) we may write

$$ N_A = N_A \Sigma\, {}_iw_A, \quad N_B = N_B \Sigma\, {}_iw_B, \quad \text{etc.}, $$

and since the total number of elements N_A, N_B, etc., of each kind cannot be varied we have

$$ N_A \Sigma\, \delta_i w_A = 0, \quad N_B \Sigma\, \delta_i w_B = 0, \quad \text{etc.} \tag{8} $$

Furthermore, let us write the total energy of the system equal to the sum of the energies of the individual elements,

$$ E = N_A \Sigma\, {}_iw_A\, {}_iE_A + N_B \Sigma\, {}_iw_B\, {}_iE_B + \cdots, $$

where ${}_iE_A$, etc., is the energy of an element of kind A with values of coördinates and momenta falling in the infinitesimal region No. iA, etc. Since E is to remain constant during the variation we may write

$$ \delta E = N_A \Sigma\, {}_iE_A \delta w_A + N_B \Sigma\, {}_iE_B \delta w_B + \cdots = 0. \tag{9} $$

The simultaneous equations (7) (8) and (9) may now be solved by the familiar method of undertermined multipliers giving us

$$ \begin{aligned} \log {}_iw_A + 1 + \lambda\, {}_iE_A + \mu_A &= 0, \quad i = 1\ 2\ 3 \cdots, \\ \log {}_iw_B + 1 + \lambda\, {}_iE_B + \mu_B &= 0, \quad i = 1\ 2\ 3 \cdots, \end{aligned} \tag{10} $$

etc.

The quantities λ, μ_A, μ_B, etc., are undetermined multipliers, where it should be specially noticed that λ is the same quantity for all the equations, while μ_A, μ_B, etc., depend on the particular kind of element in question.

For our purposes these equations can be more conveniently written in the form

$$\begin{aligned} {}_iw_A &= \alpha_A e^{-\beta\, {}_iE_A}, \\ {}_iw_B &= \alpha_B e^{-\beta\, {}_iE_A}, \\ &\text{etc.}, \end{aligned} \tag{11}$$

where e is the base of the natural system of logarithms and the constants α_A, α_B, etc., correspond to the earlier μ_A, μ_B, etc., and β corresponds to μ. These are the desired equations which describe the state of maximum probability. Thus, in accordance with the equations of definition (5), ${}_iw_A$ is the probability that any particular element kind A will have values of coördinates and momenta falling in the particular infinitesimal region, $(d_A\phi_1, d_A\phi_2, \cdots, d_A\psi_1, d_A\psi_2, \cdots)$, No. iA, when the system has attained the state of maximum probability.

Introduction of a Continuous Variable.—The quantity ${}_iw_A$ determines the number of elements that fall in the specific region No. iA. We have seen, however, in equations (11) that ${}_iw_A$ is determined by the energy corresponding to this region, and this in turn is a function of the coördinates and momenta. This makes it possible to introduce a new and convenient quantity, a variable, w_A, which is a function of these coördinates and momenta, and which gives the probability, *per unit generalized volume*, that a given element of kind A will have coördinates and momenta corresponding to the energy E_A, we may then write

$$\begin{aligned} w_A d_A\phi_1 d_A\phi_2 \cdots d_A\psi_1 d_A\psi_2 \cdots &= a_A e^{-\beta E_A} d_A\phi_1 d_A\phi_2 \cdots d_A\psi_1 d_A\psi_2 \cdots, \\ w_B d_B\phi_1 d_B\phi_2 \cdots d_B\psi_1 d_B\psi_2 \cdots &= a_B e^{-\beta E_B} d_B\phi_1 d_B\phi_2 \cdots d_B\psi_1 d_B\psi_2 \cdots, \end{aligned} \tag{12}$$

as expressions for the chance that a particular element of kind A, B, etc., will have values for coördinates and momenta falling in the infinitesimal ranges indicated.

Final Expression for the Distribution of Elements in State of Maximum Probability.—It will be noticed that the constants a_A, a_B, etc., which occur in equations (12) correspond to the μ_A, μ_B, etc., in equations (10) and hence these values will be determined by the particular kind of element A, B, etc., involved. β, on the other hand, corresponds to the earlier λ and hence its value is independent of the particular kind of element involved. In case the elements involved are the molecules of a perfect monatomic gas, it is well known that β has the value of $1/kT$,

where k is the ordinary gas constant divided by Avagadro's number, and T is the absolute temperature. Hence we may now write as our final expression for the probability that a given element of any particular kind will have values of coördinates and momenta falling within a given infinitesimal range,

$$ae^{-E/kT}d\phi_1 d\phi_2 \cdots d\psi_1 d\psi_2 \cdots, \tag{13}$$

where the value of a depends on the particular kind of element A, B, C, etc., in which we are interested, and E is the energy of one of the elements, expressed as a function of its generalized coördinates and momenta $(\phi_1\phi_2\cdots\psi_1\psi_2\cdots)$.

Two Fundamental Equations of Statistical Mechanics.—Since any element must have *some* value for its coördinates and momenta we may write the important equation,

$$\int_{\infty}\int \cdots \int_{\infty}\int \cdots ae^{-E/kT}d\phi_1 d\phi_2 \cdots d\psi_1 d\psi_2 \cdots = 1, \tag{14}$$

where the limits of the integration are such as to include all possible values of the ϕ's and ψ's.

Furthermore, it is evident that we may write for the average value of any property P of an element, the equation

$$P_{av} = \int_{\infty}\int \cdots \int_{\infty}\int \cdots ae^{-E/kT}Pd\phi_1 d\phi_2 \cdots d\psi_1 d\psi_2 \cdots, \tag{15}$$

where P is to be taken as a function of the coördinates and momenta, and the limit of integration is as above.

The General Equipartition Law.—We may now derive a very general equipartition law. Let us integrate the left-hand side of equation (14) by parts with respect to ϕ_1, we obtain

$$\left[\int \cdots \int\int \cdots ae^{-E/kT}\phi_1 d\phi_2 \cdots d\psi_1 d\psi_2 \cdots\right]_{\phi_1 = \text{lower limit}}^{\phi_1 = \text{upper limit}} - \int\int \cdots \int\int \cdots ae^{-E/kT}\phi_1 \left(\frac{-1}{kT}\right)\frac{\partial E}{\partial \phi_1}d\phi_1 d\phi_2 \cdots d\psi_1 d\psi_2 \cdots = 1. \tag{16}$$

Let us confine ourselves now to cases in which ϕ_1 becomes either zero or infinity at the two limits, and in which E becomes infinite if ϕ_1 does. Then the first term of (16) vanishes and we may write

$$\int\int \cdots \int\int \cdots ae^{-E/kT}\phi_1 \frac{\partial E}{\partial \phi_1}d\phi_1 d\phi_2 \cdots d\psi_1 d\psi_2 \cdots = kT. \tag{17}$$

In accordance with (15), however, this gives us the average value of $[\phi_1(\partial E/\partial \phi_1)]$ and hence, applying similar consideration to the other coördinates and momenta, we may now write as our general equipartition law:

$$\left[\phi_1 \frac{\partial E}{\partial \phi_1}\right]_{av} = \left[\phi_2 \frac{\partial E}{\partial \phi_2}\right]_{av} \cdots = \left[\psi_1 \frac{\partial E}{\partial \psi_1}\right]_{av} = \left[\psi_2 \frac{\partial E}{\partial \psi_2}\right]_{av} = \cdots = kT, \quad (18)$$

and this law will apply in all cases in which the above condition as to the limits of integration is fulfilled.

The General Equation for the Partition of Energy.—In the particular case that the energy is a homogeneous quadratic function of the coördinates and momenta the above equation (18) will evidently reduce to the value $\frac{1}{2}kT$ for the energy associated with each coördinate or momentum, which is the familiar principle of the equipartition of energy.

Whatever may be the relation, however, between energy and the coördinates and momenta, we may obtain its average value for a given kind of element with the help of equation (15), which permits us to write

$$E_{av} = \int\int \cdots \int\int \cdots a e^{-E/kT} E d\phi_1 d\phi_2 \cdots d\psi_1 d\psi_2 \cdots. \quad (19)$$

In order to eliminate the constant a we may divide (19) by (14) and obtain,

$$E_{av} = \frac{\int\int \cdots \int\int \cdots e^{-E/kT} E d\phi_1 d\phi_2 \cdots d\psi_1 d\psi_2 \cdots}{\int\int \cdots \int\int \cdots e^{-E/kT} d\phi_1 d\phi_2 \cdots d\psi_1 d\psi_2 \cdots}. \quad (19a)$$

We may now apply equations (18) and (19*a*) to obtain information as to the partition of energy in a number of interesting cases.[1]

PART II. MISCELLANEOUS APPLICATIONS.

Gas Subjected to Gravity.—For the first application of our equations let us consider a monatomic gas subjected to the action at gravity, *in a tube of infinite length.* Considering the Z axis as vertical we can write for the energy of any given molecule,

$$E = mgz + \frac{m\dot{x}^2}{2} + \frac{m\dot{y}^2}{2} + \frac{m\dot{z}^2}{2},$$

where z is the height of the molecule above the surface of the earth. In terms of the components of momentum, our expression for energy may be rewritten:

$$E = mgz + \frac{1}{2m}\psi_x^2 + \frac{1}{2m}\psi_y^2 + \frac{1}{2m}\psi_z^2,$$

[1] In applying these equations it is to be noticed that we do not need to make the elements into which we divide our statistical system agree with what are ordinarily thought of as the physical elements of the system. Thus if our system is a quantity of a monatomic gas, instead of taking each atom with its three positional coördinates and its three momenta as an element we may take these variables as belonging to six different elements. Indeed it is obvious, from our methods of deduction, that we shall need to class coördinates and momenta together as belonging to the same element only in groups large enough so that any given coördinate momentum will not appear in the expression for the energy of more than one of our elements.

where the components of momentum are given by the equations

$$\psi_x = m\dot{x}, \quad \psi_y = m\dot{y}, \quad \psi_z = m\dot{z}.$$

Applying our equipartition equation (18) we obtain

$$[mgz]_{av} = \left[\frac{1}{m}\psi_x^2\right]_{av} = \left[\frac{1}{m}\psi_y^2\right]_{av} = \left[\frac{1}{m}\psi_z^2\right]_{av} = kT,$$

or, introducing the equations defining momenta, we obtain

$$[mgz]_{av} = kT, \quad \left[\frac{m\dot{x}^2}{2}\right]_{av} = \left[\frac{m\dot{y}^2}{2}\right]_{av} = \left[\frac{m\dot{z}^2}{2}\right]_{av} = \tfrac{1}{2}kT.$$

And we see that according to our equipartition law, the average potential energy per molecule is *twice* as great as the average kinetic energy in any direction.

This is a particularly simple case of a deviation from the principle of the equipartition of energy, and of course it could have been shown by methods which have long been familiar, that the average potential energy per molecule is twice as great as the average component of kinetic energy. It should be specially noticed that this is a deviation from the principle of the equipartition of energy which bears no relation to those which have more recently been discovered and studied by the quantum theory.

The Energy Any Simple Power of the Coördinates.—The above deviation from the equipartition of energy was due to the fact that the potential energy of these molecules was proportional to the first power instead of to the square of the coördinate involved. We may point out with the help of equation (18) what the general relation will be. If the energy for a given elementary coördinate or momentum is proportional to the nth power of that invariable,

$$E = c\phi^n, \tag{20}$$

then by (18) we shall have

$$E_{av} = \frac{kT}{n}.$$

Thus, for example, if we had in our system oscillating elements in which the restoring force, instead of following Hook's law, was proportional to the square of the displacement, then the average potential energy of these oscillators would be $\frac{1}{3}kT$ instead of the familiar $\frac{1}{2}kT$.

These considerations will be of value in case we find it convenient to express the energy of an element by an empirical formula of the form

$$E = a + b\phi + c\phi^2 + d\phi^3 + \cdots.$$

Relativity Mechanics.—As another example of a deviation from the

principle of the equipartition of energy, we may consider a monatomic gas whose molecules are considered as particles, obeying the new "relativity" laws of motion instead of Newton's laws of motion, which we now know are only the approximate form assumed by the correct laws of motion at low velocities.

According to these new laws of motion we must write for the components of momentum of a particle:

$$\psi_x = \frac{m_0\dot{x}}{\sqrt{1 - \frac{\dot{x}^2 + \dot{y}^2 + \dot{z}^2}{c^2}}},$$

$$\psi_y = \frac{m_0\dot{y}}{\sqrt{1 - \frac{\dot{x}^2 + \dot{y}^2 + \dot{z}^2}{c^2}}}, \tag{21}$$

$$\psi_z = \frac{m_0\dot{z}}{\sqrt{1 - \frac{\dot{x}^2 + \dot{y}^2 + \dot{z}^2}{c^2}}},$$

where m_0 is the mass of the particle at rest and c is the velocity of light.

For the kinetic energy of the particle we may write

$$E = \frac{m_0c^2}{\sqrt{1 - \frac{\dot{x}^2 + \dot{y}^2 + \dot{z}^2}{c^2}}}, \tag{22}$$

a quantity which except for a constant reduces to $\frac{1}{2}m_0(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$ at low velocities. In terms of the momenta we may rewrite this expression for the kinetic energy in the form

$$E = c\sqrt{c^2m_0^2 + \psi_x^2 + \psi_y^2 + \psi_z^2}. \tag{23}$$

Applying equation (18) we obtain

$$\left[\psi_x \frac{c\psi_x}{\sqrt{c^2m_0^2 + \psi_x^2 + \psi_y^2 + \psi_z^2}}\right]_{av} = \left[\psi_y \frac{c\psi_y}{\sqrt{c^2m_0^2 + \psi_x^2 + \psi_y^2 + \psi_z^2}}\right]_{av}$$
$$= \text{etc.} = kT,$$

and introducing our previous equations, this may be written

$$\frac{1}{2}\left[\frac{m_0\dot{x}^2}{\sqrt{1 - \frac{\dot{x}^2 + \dot{y}^2 + \dot{z}^2}{c^2}}}\right]_{av} = \frac{1}{2}\left[\frac{m_0\dot{y}^2}{\sqrt{1 - \frac{\dot{x}^2 + \dot{y}^2 + \dot{z}^2}{c^2}}}\right]_{av}$$
$$= \frac{1}{2}\left[\frac{m_0\dot{z}^2}{\sqrt{1 - \frac{\dot{x}^2 + \dot{y}^2 + \dot{z}^2}{c^2}}}\right]_{av} = \tfrac{1}{2}kT. \tag{24}$$

We thus see that in relativity mechanics we have the equipartition of a function which reduces to the kinetic energy $\frac{1}{2}m_0\dot{x}^2$, etc., at low velocities, but at high velocities is not even the same as the *relativity* expression for energy.[1]

These few examples are sufficient to illustrate the application of our methods, in fields other than those treated by the quantum theory. Let us now turn our attention to the partition of energy between the different modes of vibration of a hohlraum.

PART III. APPLICATION TO THE HOHLRAUM.

The Idea of Quanta.—In developing a theory of the hohlraum, we may base our considerations on the fact that radiant energy is known to be absorbed and evolved substantially in quanta of the amount $h\nu$, where h is Planck's new constant and ν is the frequency of the radiation involved. This is an experimental fact, illustrated most simply by the photo-electric effect and the inverse photo-electric effect, and is certainly the expression of a fundamental characteristic of radiant energy.

This important fact can be incorporated in our new system of statistical mechanics by assuming that the energy associated with a given mode of vibration in the hohlraum increases with the amplitude of the vibrations in a relatively discontinuous fashion by amounts of the magnitude $h\nu$. If ϕ is a generalized coördinate which determines the displacement for a given mode of vibration and ψ is the corresponding generalized momentum, then in the older dynamics the energy associated with the mode would have been given by the formula

$$E = k\phi^2 + l\psi^2, \tag{25}$$

where k and l are constants. According to this formula the potential energy $k\phi^2$ increases continuously with the square of the displacement and the kinetic energy $l\psi^2$ with the square of the momentum.

In our new dynamics let us assume that the energy is practically zero until $k\phi^2 + l\psi^2$ reaches the value $h\nu$ and that it then increases with great suddenness to the value $h\nu$, remaining again practically constant until it increases to the amount $2h\nu$, when $k\phi^2 + l\psi^2$ itself reaches the value $2h\nu$, and so on, for following intervals, the energy attaining successively the values $3h\nu$, $4h\nu$, etc.

Expression for Energy.—Such a relation between energy and the coordinates can be expressed algebraically by the equation

$$E = h\nu\{e^{-[h\nu/(k\phi^2+l\psi^2)]^n} + e^{-[2h\nu/(k\phi^2+l\psi^2)]^n} + e^{-[3h\nu/(k\phi^2+l\psi^2)]^n} + \cdots\}, \tag{26}$$

[1] This new equipartition law for the special case of relativity mechanics was first derived by the author, Phil. Mag., *28*, 583 (1914). The same article or an earlier one by Jüttner, Ann. d. Physik, *34*, 856 (1911), may be consulted for an investigation of the actual energy partition in this case.

where n is some number large enough so that the exponents of e change suddenly from minus infinity to zero when $k\phi^2 + l\psi^2$ assumes the successive values $h\nu$, $2h\nu$, $3h\nu$, etc. If n were itself given the value infinity, the energy would increase in absolutely abrupt steps of the magnitude $h\nu$. It is not our belief, however, that the energy changes absolutely abruptly at the points in question, since if this were the case the whole application of our statistical mechanics would be fallacious, since it is based on the Hamiltonian equations which presuppose a motion which is at least continuous when regarded from a fine-grained enough point of view. Furthermore it is not to be supposed that the *precise* relation between energy and the coördinates is necessarily given by equation (26). The expression presented or any other which makes the energy increase in the way described, substantially in quanta, is quite suitable for the purposes of integration which we have in view, but might not be suitable, if we should desire to differentiate (26) for the purpose of determining the equations of motion in the Hamiltonian form.

Before leaving the discussion of equation (26), we should point out that ν is the frequency of the particular mode of vibration involved and h is Planck's new universal constant which has the magnitude 12.83×10^{-27} erg $\times$ seconds, so that even with a frequency of many billions per second, the energy would apparently increase with the amplitude of vibration in a perfectly continuous fashion in accordance with the simple equation $E = k\phi^2 + l\psi^2$, which has been made familiar by experimentation with those everyday vibrating systems whose frequencies are low.

Partition of Energy in the Hohlraum.—Having described the relation between energy and the coördinates which we believe to exist, let us proceed to determine the partition of energy in the hohlraum, by the methods which we have developed in the earlier part of the article. In accordance with equation (19a) we may write for the average energy associated with a given mode of vibration,

$$E_{av} = \frac{\int\int e^{-E/kT} E d\phi d\psi}{\int\int e^{-E/kT} d\phi d\psi}.$$

In order to evaluate these integrals for our particular case, we may note in accordance with equation (26), that the energy E will have the value zero for all values of ϕ and ψ which lie inside the ellipse $k\phi^2 + l\psi^2 = h\nu$, the value $h\nu$ for all values of ϕ and ψ falling in the space between this ellipse and the concentric one $k\phi^2 + l\psi^2 = 2h\nu$, and so on for successive concentric ellipses. This permits us to rewrite the above equation in the form

$$E_{av} = \frac{\iint\limits_{0<k\phi^2+l\psi^2<h\nu} e^{\circ}0 d\phi d\psi + \iint\limits_{h\nu<k\phi^2+l\psi^2<2h\nu} e^{-h\nu/kT} h\nu d\phi d\psi + \iint\limits_{2h\nu<k\phi^2+l\psi^2<3h\nu} e^{-2h\nu/kT} 2h\nu d\phi d\psi + \cdots}{\iint\limits_{0<k\phi^2+l\psi^2<h\nu} e^{\circ} d\phi d\psi + \iint\limits_{h\nu<k\phi^2+l\psi^2<2h\nu} e^{-h\nu/kT} d\phi d\psi + \iint\limits_{2h\nu<k\phi^2+l\psi^2<3h\nu} e^{-2h\nu/kT} d\phi d\psi + \cdots}.$$

Since the area enclosed by the successive ellipses increases by equal steps of the amount $(\pi h\nu/\sqrt{kl})$, the above expression can be reduced to

$$E_{av} = \frac{h\nu(e^{-h\nu/kT} + 2e^{-2h\nu/kT} + 3e^{-3h\nu/kT} + \cdots)}{1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + e^{-3h\nu/kT} \cdots)},$$

which upon division is seen to be

$$E_{av} = \frac{h\nu}{e^{h\nu/kT} - 1}, \qquad (27)$$

which is the well-known expression, assumed by the quantum theory upon *empirical* grounds, as the average energy for a mode of vibration of frequency ν. The result is of significance in showing that our generalized dynamics, in which the energy can be any function of the coördinates and momenta, leads to a statistical mechanics broad enough to account for the actual partition of energy found in the hohlraum.

Emission of Energy by Quanta.—Before leaving this discussion we should point out that the relation (26) between energy and the generalized coördinates which we have chosen, not only accounts, as we have just seen, for the partition of energy in the hohlraum, but also explains the photo-electric and the inverse photo-electric effects. This arises from the fact that in accordance with the fundamental structure of our system of statistical mechanics all microscopic states for a given mode of vibration are equally probable, and since the vast majority of these microscopic states correspond to an energy content, which is an exact multiple of $h\nu$, we shall expect generally to find radiant energy absorbed and emitted in amounts $h\nu$ or some multiple thereof.

Nature of the Electromagnetic Field.—It is, further, to be pointed out, if we are permitted to trespass for a moment in a field of uncertain speculation, that our relation (26) between energy and the coördinates indicates a somewhat fibrous structure for the electromagnetic field when viewed from a fine-grained enough, and not *too* fine-grained, point of view. It seems to the writer, that this conclusion might furnish support to those theories of the atom[1] which assign very definite positions,

[1] See, for example, Lewis, J. Amer. Chem. Soc., *38*, 762 (1916).

with reference to the positive nucleus, to those electrons which determine the chemical properties of the atom, since the fibrous structure of the electromagnetic field surrounding the positive nucleus might easily provide rather definite pockets where these electrons would find their positions of equilibrium.